

# REPORT DOCUMENTATION PAGE-

Form Approved  
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE  
12/28/95

3. REPORT TYPE AND DATES COVERED  
Final Technical Report

4. TITLE AND SUBTITLE

High Temperature Superconducting Compounds

5. FUNDING NUMBERS

AFOSR Grant  
F49620-93-1-0076

61102 F  
2305 /GS

6. AUTHOR(S)

Allen M. Goldman

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Minnesota  
Office of Research & Technology Transfer Administration  
1100 Washington Avenue South, Suite 201  
Minneapolis, MN 55415-1226

8. PERFORMING ORGANIZATION  
REPORT NUMBER

AFOSR-TR-96  
6016

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NE  
110 Duncan Ave., Suite B115  
Bolling AFB, DC 20332-0001

10. SPONSORING/MONITORING  
AGENCY REPORT NUMBER

F49620-93-1-0076

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release;  
distribution unlimited.

12b. DISTRIBUTION CODE

19960201 141

13. ABSTRACT (Maximum 200 words)

This report describes work conducted under AFOSR Grant #F49620-93-1-0076. This program was concerned with films of high- $T_c$  superconducting compounds with the objective of elucidating the underlying mechanism of the superconductivity as well as developing processes and structures of technological significance. The research was focused on the fabrication and characterization of films grown using ozone-assisted molecular beam epitaxy (MBE). The most significant development was the successful achievement of the so-called block-by-block deposition technique. In addition to superconducting films of high quality, we have grown nonsuperconducting oxides which exhibit the phenomenon which has been called colossal magnetoresistance (CMR), and insulating oxides which may be useful in preparing planar tunneling junctions. We have also carried out a major study of the symmetry of the pairing state through an investigation of the transverse Meissner effect. Its result does not support d-wave pairing. Other accomplishments include characterization of the noise spectral density of superconducting films in a magnetic field, modeling of the electric field effect in high- $T_c$  films, studies of tunneling spectra using low temperature scanning tunneling microscopy, and the study of the penetration depth near the superconducting transition.

14. SUBJECT TERMS

Superconductivity, tunneling, thin films, molecular beam epitaxy

15. NUMBER OF PAGES

25

16. PRICE CODE

17. SECURITY CLASSIFICATION  
OF REPORT

18. SECURITY CLASSIFICATION  
OF THIS PAGE

19. SECURITY CLASSIFICATION  
OF ABSTRACT

20. LIMITATION OF ABSTRACT

Final Technical Report

**HIGH TEMPERATURE SUPERCONDUCTING COMPOUNDS**

**AFOSR Grant No. F49620-93-1-0076**

1 December 1992 through 30 November 1995

27 December 1995

School of Physics and Astronomy  
University of Minnesota  
116 Church St. SE  
Minneapolis, Minnesota 55455

Allen M. Goldman, Principal Investigator

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## 1.0. Summary

This report describes the results of research during the period 1 December 1992 to 30 November 1995 conducted under AFOSR Grant No. F49620-93-1-0076. This program was primarily concerned with films of high- $T_c$  superconducting compounds with the ultimate objective of elucidating the underlying mechanism of the superconductivity of these materials as well as developing processes and structures of technological significance.

The work carried out was focused on activities involving the fabrication and characterization of thin films. All films which were studied were grown using the technique of ozone-assisted molecular beam epitaxy (MBE) using thermal sources (Berkley et al., 1988). This approach has advantages over more commonly used techniques such as sputtering and laser ablation in providing a greater degree of control of the growth process which can be monitored *in situ* in real time using reflection high energy electron diffraction (RHEED). In contrast with laser ablation, there are no semi-macroscopic particles present in MBE-grown films, which greatly enhances the prospects of passivating and insulating surfaces.

The most significant development in the areas of film growth was the successful introduction of shuttered growth to improve the quality and physical properties of high- $T_c$  MBE grown films by forming them using the technique of block-by-block deposition (BBD). In addition to producing superconducting compounds, we have used this technique to grow nonsuperconducting oxides which exhibit the phenomenon which has been called colossal magnetoresistance (CMR). The materials we have grown using the BBD technique are among the smoothest and most highly ordered oxide films produced anywhere. The CMR materials possess a magnetic phase transition coupled to a semiconductor-metal transition. They are potentially technically important in the context of magnetic sensors of all types, and there is the possibility of producing heterostructures and tunneling junctions of these materials with the superconducting cuprates. In addition to the CMR materials we have produced cuprate-compatible insulating oxides which may be especially useful in preparing planar cuprate tunneling junctions. The above accomplishments should facilitate various strategies directed at producing high-quality tunneling junctions, the growth of planar junctions with epitaxial insulators, and the preparation of in-line junctions and photoconductive structures by surface properties modification using scanning tunneling microscopy (STM). It will also provide films of high quality for additional fundamental studies of ultrathin superconducting films.

We have also succeeded in carrying out a major study of the symmetry of the pairing state through an investigation of the transverse Meissner effect. This measurement can in principle determine whether there are nodes in the order parameter as would be expected in the case of certain pairing state symmetries, such as the d-wave symmetry. This work will be continued and

enhanced during the next grant. Block-by-block deposition of oxides, and the pairing-state studies are the most important research activities carried out under this grant.

There were a number of other accomplishments which should also be noted. These investigations will not be continued in the renewal period, either because they have been completed, or because they do not fit into the coherent, smaller program which was funded. The work includes characterization of the noise spectral density of superconducting films in a magnetic field, modeling of the electric field effect in high- $T_c$  films, studies of tunneling spectra obtained using low temperature scanning tunneling microscopy, and the study of the penetration depth near the superconducting transition. The latter investigation suggests that the penetration depth has a mean field temperature dependence near the transition in contrast with some other experimental work which suggested that it was XY-like. The analysis of our data depends crucially on the inclusion of boundary effects on the electromagnetic field and induced currents in the film. The mean-field behavior of the penetration depth is believed to be a consequence of the coupling of superconducting fluctuations with electromagnetic field fluctuations in the context of the XY model.

Below we list the papers published under this grant along with those which were submitted for publication before the termination date.

## 2.0 Publications Supported by This Grant

1. "Mechanism for Electric Field Effects Observed in  $YB_2Cu_3O_{7-x}$  Films," N. Chandrasekhar, Oriol T. Valls, and A. M. Goldman, *Phys. Rev. Lett.* **71**, 1079 (1993).
2. "The Interplay between Antiferromagnetism and Superconductivity in Disordered Ultrathin High- $T_c$  Films," K. M. Beauchamp, T. Wang, G. C. Spalding, and A. M. Goldman, *Physica A* **200**, 287 (1993).
3. "Classes of Superconductor-Insulator Transitions in High- $T_c$  Films," K. M. Beauchamp, G. C. Spalding, T. Wang, and A. M. Goldman, *Physica B* **194-196**, 2321 (1994).
4. "Probing Vortex Kinetics in High- $T_c$   $Y(Dy)Ba_2Cu_3O_7$  Thin Films with Noise," Edmund R. Nowak, N. E. Israeloff, V. S. Achutharaman, and A. M. Goldman, , *Physica B* **194-196**, 2303 (1994).
5. "A Monte Carlo Study of Aging Effects Observed in  $(RE)Ba_2Cu_3O_{7-x}$  Films," N. Chandrasekhar, Oriol T. Valls, and A. M. Goldman, *Physica B* **194-196**, 2295 (1994).
6. "A Mechanism for Electric Field Effects Observed in  $(RE)Ba_2Cu_3O_{7-x}$  Films," N. Chandrasekhar, Oriol T. Valls, and A. M. Goldman, *Physica B* **194-196**, 2297 (1994).
7. "Charging Effects Observed in  $YBa_2Cu_3O_{7-x}$  Films: Influence of Oxygen Ordering," N. Chandrasekhar, Oriol T. Valls, and A. M. Goldman, *Phys. Rev. B* **49**, 6220 (1994).

8. "Compound Geometric Resonances in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  Single Crystals," Jin-Xiang Liu, Stephen W. Pierson, G.C. Spalding, Ji-Chun Wan, and A.M. Goldman, *Physica B* **194-196**, 2233 (1994).
9. "Magneto-Fingerprinting Superconducting Films: Vortex Dynamics and Meso-Scale Disorder," Edmund R. Nowak, N. E. Israeloff, and A. M. Goldman, *Phy. Rev.* **B49**, 10047 (1994).
10. "Origin of RHEED Intensity Oscillations During the Growth of  $(\text{Y}, \text{Dy})\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$  Thin Films," V. S. Achutharaman, N. Chandrasekhar, Oriol T. Valls, and A. M. Goldman, *Phys. Rev.* **B50**, 8122 (1994)..
11. "A Transverse Magnetization Study of the Pairing State of the High- $T_c$  Superconductor  $\text{LuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ," J. Buan, Branko P. Stojkovic, N. E. Israeloff, A. M. Goldman, C. C. Huang, Oriol T. Valls, J. Z. Liu, and Robert Shelton, *Phys. Rev. Lett.* **72**, 2632 (1994).
12. "Temperature Dependence of the Penetration Depth of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  Films near  $T_c$ ," Z .H. Lin, G. C. Spalding, A. M. Goldman, B. F. Bayman, and O. T. Valls, accepted for publication in *Europhysics Letters*.
13. "Chain Oxygen Dynamics in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  under Applied Electric Fields and Related Phenomena," N. Chandrasekhar, Oriol T. Valls, and A. M. Goldman, *Modern Physics Letters B* **8** 1863 (1994).
14. "Reply to "Comment on Mechanism for Electric Field Effects Observed in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  Films," N. Chandrasekhar, Oriol T. Valls, and A. M. Goldman, *Phys. Rev. Lett.* **73**, 1562 (1994).
15. "Growth of La-Ca-Mn-O films by ozone-assisted molecular beam epitaxy," V. S. Achutharaman, P.A. Kraus, V.A. Vas'ko, C.A. Nordman, and A.M. Goldman, , *Appl. Phys. Lett.* **67**, 1019 (1995).
16. "Determination of the Pairing State of High- $T_c$  Superconductors through Measurement of the Transverse Magnetization," J. Buan, Branko P. Stojkovic, N.E. Israeloff, A. M. Goldman, C.C. Huang, Oriol T. Valls, J. Z. Liu, and Robert Shelton, *Physica C* **235-240**, 1893 (1994).
17. "Experimental Investigation of the Pairing State of High Temperature Superconductors," J. Buan, T. Jacobs, C. R. Shih, Branko P. Stojkovic, Nathan Israeloff, J-Z. Liu, A. M. Goldman, C. C. Huang, Robert Shelton, S. Sridhar, Oriol T. Valls, and H. D. Yang, submitted to *Phys. Rev. B*.

18. "UltrasMOOTH, highly ordered, thin films of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3\pm d}$ " V. A. Vas'ko, C. A. Nordman, P. A. Kraus, V. S. Achutharaman, A. R. Ruosi, and A. M. Goldman, submitted to Appl. Phys. Lett.

### 3.0. Selected Details of Accomplishments

#### 3.1. Block-by-Block Deposition of High- $T_c$ Cuprates and Other Oxide Materials

The growth of cuprate films is extremely complex as it involves the combination and reaction of four or more elements. In the case of the growth of  $\text{DyBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (DBCO) films, this leads to the possibility of a multitude of phases such as  $\text{BaCu}_2\text{O}_2$ ,  $\text{Dy}_2\text{O}_3$ ,  $\text{DyCuO}_2$  and  $\text{Cu}_2\text{O}$  forming and remaining stable. Hence, it is crucial to control or tailor the growth to avoid the formation of undesired precipitates to obtain the highest quality film in terms of surface morphology and defects. Recent work by the group at IBM Zurich, (Locquet *et al.* (1994) and Locquet and Machler (1994)) provides a way out of these difficulties. These workers achieved surface roughnesses of the order of  $\pm 1$  unit cell in DBCO films grown by MBE using the technique of "block-by-block" deposition which is a sequential technique. The method involves growing films along a thermodynamically optimum path rather than layer-by-layer. The idea is that during the deposition of any block only one reaction takes place. A block grows two dimensionally and covers the full surface. Block sequences leading to stable phases are avoided, but the reaction path has only one final product. This has been accomplished for the 123 compounds, and as will be indicated below, we have also succeed in carrying it out for the growth of the manganite compounds as well.

Procedures in which growth is interrupted after the formation of one or two unit cells to let the surface recover and attain its equilibrium configuration are relatively well known. When they have been carried out in the growth of 1-2-3 materials, *in-situ* reflection high energy electron diffraction (RHEED) studies indicate that although the RHEED intensity recovers to almost its initial value during every interruption, it never really attains its previous value. The RHEED intensity gradually decays indicating the development of an increasingly rough surface with higher surface step density. In the case of film growth by sputtering, a technique called NACHOS, in which the sample is vibrated with respect to the plasma has been shown to produce films with roughness of the order of an unit cell. Both the above mentioned techniques involve the simultaneous deposition of all of the elemental constituents of the film being grown.

The block-by-block deposition (BBD) technique is an approach to film growth in which the different complexes or species which constitute the compound are deposited in succession, but not



at the same time. Another so-called sequential technique is atomic layer-by-layer molecular beam epitaxy (ALLMBE). Since both BBD and ALLMBE attempt to control reactions occurring on the surface, this general approach has been called Reaction Controlled Epitaxy (RCE).

Figure 1 is the proposed phase diagram of the Dy-Ba-Cu-O system under thin film deposition conditions. Each of the sequential growth methods takes a different path through the phase diagram. It is hence imperative to choose a path that does not allow the formation of

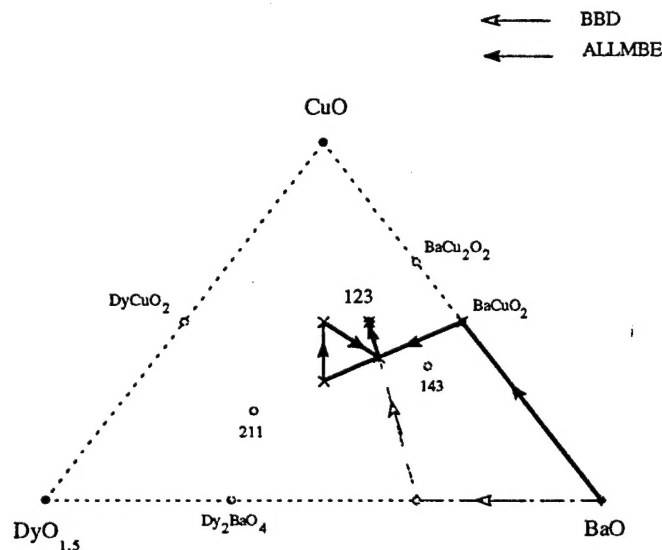


Fig. 1. Proposed phase diagram for film growth of the Dy-Ba-Cu-O system. The paths taken for the ALLMBE sequence and the BBD sequence are marked on the diagram.

undesired, stable phases. The sequence Ba-Cu-Dy-Cu-Ba-Cu in the case of ALLMBE and Ba-Dy-Cu in the case of BBD have been found to produce films with the least defects. Both these paths are illustrated in the phase diagram, Fig. 1. It can be clearly seen that the BBD route avoids the formation of all the possible stable phases marked in the diagram.

We have grown  $\text{DyBa}_2\text{Cu}_3\text{O}_{7-x}$  films of different thickness (10 - 100 unit cells) on  $\text{SrTiO}_3$  (100) and  $\text{CeO}_2$ /sapphire substrates using ozone-assisted molecular beam epitaxy employing BBD. The growth parameters such as the substrate temperature and the ozone partial pressure were varied to obtain an understanding of their influence on the kinetic processes occurring on the surface during the deposition of different blocks in the sequence. The growth was continuously monitored by *in-situ* RHEED and the images were recorded on tape using a CCD camera.



The films were characterized using high resolution X-ray diffraction. X-ray reflectivity and rocking curve analyses were performed using a Philips MRD high resolution diffractometer to obtain an idea of the structural perfection and the surface morphology of these films. The chemical compositions were analyzed using inductively-coupled plasma mass spectroscopy, and were found to be consistent with Rutherford backscattering analyses. STM studies were done to study the surfaces of these films, i. e., to investigate the presence or absence of usual defects such as screw dislocations, and also to corroborate the roughness values obtained from x-ray reflectivity and Bragg scan finite thickness oscillation studies.

RHEED images were always streaked during the deposition of Ba indicating a smooth surface. However, the RHEED image and the hence the surface morphology after the deposition of Dy seem to depend on the partial pressure of ozone. For films grown at higher ozone pressures, the lines remain streaked through to the end of the deposition, whereas the pattern for films grown at lower pressures is a spotted square, a result similar to that reported for BBD deposition using atomic oxygen by the IBM group (Locquet et al, 1994). RHEED images are streaked at the end of the deposition of the Cu layer which corresponds to the termination of a unit cell layer.

Figure 2 is a low angle  $2\theta$ - $\omega$  reflectivity scan of a 470 Å thick film grown by BBD. Koenig, or thickness fringes are clearly visible indicating that the film-air and the film-substrate interfaces are very smooth with roughness of the order of a unit cell. These oscillations have even been observed for an 85 unit cell thick film indicating that the films are smooth up to thicknesses the order of 1000 Å. A  $2\theta$ - $\omega$  scan of the (001) peak of DBCO for the same film is shown in Fig.3. Finite size oscillations can again be observed which further confirms that the thickness fluctuations are of the order of an unit cell. Very few observations of these finite size oscillations have been made for any 123-type films.

Figure 4 shows the rocking curve obtained for the (001) DBCO peak. The full-width at half-maximum (FWHM) of the peak is  $\approx 0.07^\circ$  which is about an order of magnitude higher than that of the substrate. It is hence reasonable to assume that all the broadening is due to the film and is not instrumental. The FWHM is lower than *any* value that has been published in the literature for these materials.

The roughness estimates from the X-ray reflectivity and Bragg peak scans agree extremely well with those from STM studies. From the STM pictures of a 1000 Å film, described in the next

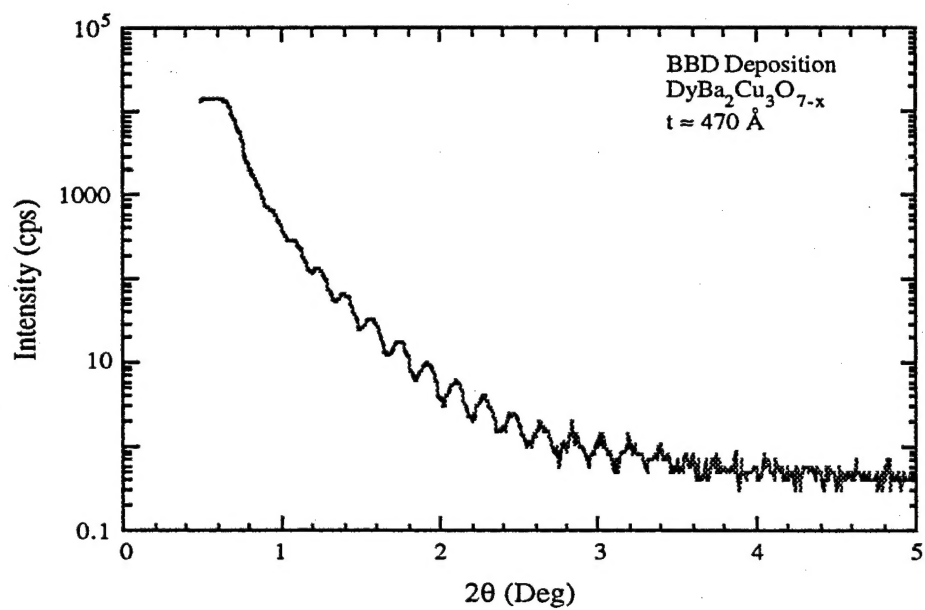


Fig. 2. X-ray reflectivity scan of a 470Å thick DBCO film grown by BBD.

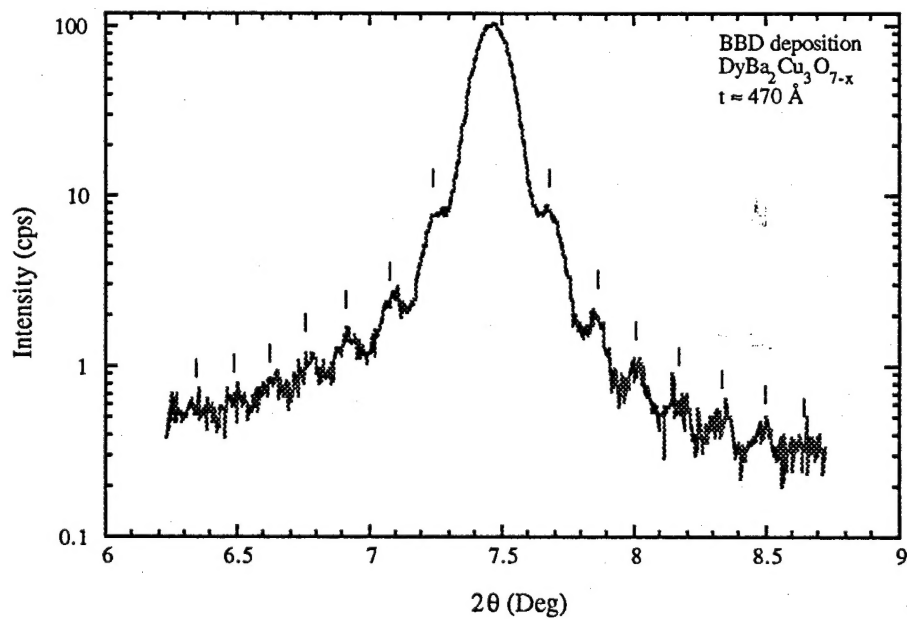


Fig. 3.  $2\theta$ - $\omega$  scan of the (001) DBCO Bragg peak. Finite size oscillations are clearly visible.

section on STM patterning, it is found that the surface consists mainly of terraces. No spirals have been observed in the STM scans so far. More studies are in progress to verify the absence of screw dislocations or spiral grains. Ion channeling studies are also in progress to obtain a different parameter, the ion channeling yield, which can also be used to characterize the structural perfection of these films.

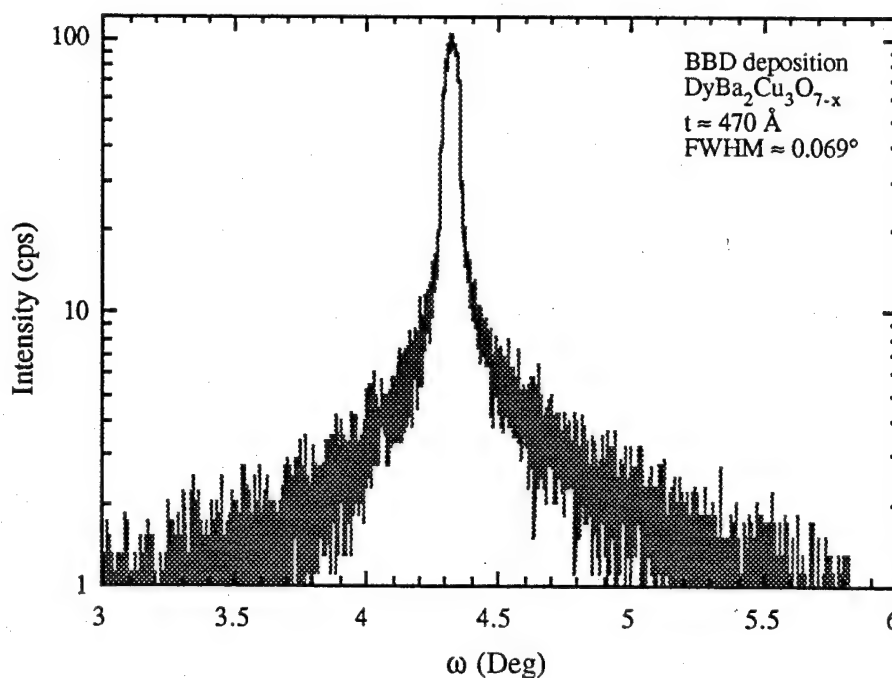


Fig. 4. Rocking curve of the (001) peak. The FWHM is around  $0.07^\circ$  which is the lowest reported in the literature.

As seen above, we have implemented the BBD technique and carried out a detailed study of the resultant films. Our results go considerable beyond those of Locquet and Machler and will be submitted for publication shortly. This publication will include our most recent results which involve the successful growth of  $\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$  films of very high quality using the BBD technique.

### 3.2. Tunneling Structures with High- $T_c$ Materials

We have been attempting to fabricate high- $T_c$  tunneling junctions through the development of a new technique for writing in-line junctions. Such junctions with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  electrodes have been produced by direct electron beam writing (Tolpygo et al., 1993), and by

scanning tunneling microscope (STM) etching (Heyvaert et al., 1992), an approach which involves some combination of field-induced evaporation, mechanical milling and STM-induced thermal diffusion. We are attempting a variant on this theme which takes advantage of our experience with ultrathin films. We have observed that films of the order of 30-50 Å in thickness are stable, whereas thinner films are susceptible to degradation by oxygen out-diffusion. We are currently attempting to write in-line junctions on ultrathin films which are just thick enough to be stable. Under the influence of the electric field from the STM tip in the tunneling, rather than in the field emission mode, we believe that we can produce a stable damage track, or oxygen deficiency track which is much narrower than that produced by electron beam writing, or by STM writing in the field emission mode which is the mode usually used for surface modification.

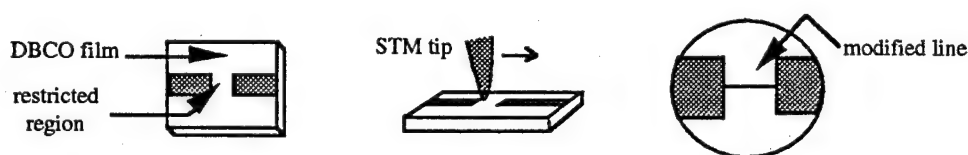


Fig. 5. Schematic of junction writing scheme.

Ideally we would like to produce a line which is oxygen deficient which is several tens of Å wide, and which is stable against re-oxygenation by diffusion at room temperature. A schematic of the approach is shown above.

As depicted, a thin film of  $\text{DyBa}_2\text{Cu}_3\text{O}_{7.8}$  (DBCO) is deposited with a restricted region patterned using conventional processes. A line is then drawn across the restricted region using a scanning tunneling microscope (STM) appropriately biased such that the DBCO is altered in composition and is no longer a superconductor. The result then is a superconductor / barrier/ superconductor junction in the plane of the substrate.

The important research concerns are:

- 1.) Determining film thickness that fully exploits the depth of STM-altered DBCO.
- 2.) Creating high quality, uniform, thin films of DBCO using BBD techniques described above.
- 3.) Determining the effects of the STM on the DBCO.
- 4.) Characterizing the junctions that are produced.
- 5.) Developing a more versatile patterning process for the restricted regions.
- 6.) Exploring the possibilities of in-plane superconducting junction arrays and devices (including perhaps single-electron devices).

Examining the effects of STM scanning on the DBCO films has constituted the bulk of our research efforts supported by this grant. Some very encouraging and significant results have been observed. Thus far, surface (STM) examination of thicker (500Å) films grown by BBD technique

reveal a surface which is terraced, but the growth does not appear as spirals (which have been associated with screw dislocations). We are preparing to look at films thinner than  $100\text{\AA}$ , and expect the surface to be even smoother since surface roughness generally increases with thickness.

We have observed interesting surface modification effects in our films brought about by the STM. The surfaces appear to be both imaged and *modified* by the STM. Some of the terraces vanish. It seems plausible to assume that the disappearing terraces are in fact still there, but that the oxygen has been depleted from the  $\text{DyBa}_2\text{Cu}_3\text{O}_7$  structure. The  $\text{DyBa}_2\text{CuO}_6$  structure is known to be a semiconductor, thus, this material would be relatively undetectable if the semiconductor gap voltage were greater than the tunneling probe voltage. The tunneling would terminate in the lower, unmodified DBCO layers which are metallic-like at room temperature. Further studies are being initiated to examine this idea by allowing the modified region to remain for some time at room temperature before scanning again; if oxygen removal is responsible, then diffusion of oxygen back into the depleted layer from the rest of the film may cause a portion of a terrace to reappear.

Some STM-damaged regions show a transient response to light which does not appear to be bolometric in nature. The films that have larger damaged areas across the restricted region are cooled down to  $4.2\text{K}$  and their in-plane resistance is measured while subjecting the samples to pulses of light. In some, the resistance appears to decrease slightly during exposure. These phenomena will be investigated further as we pursue this approach to junction fabrication.

### 3.3. The Low Frequency AC Impedance of High- $T_c$ Films

We have had an on-going effort at measuring the impedance of high- $T_c$  superconducting films using ac-impedance measuring techniques, in particular employing the two-coil method of Jeanneret and collaborators (1989). This is a scheme in which the drive and pickup coils are on the same side of the film. Our studies of the penetration depth at low temperatures have not revealed any features of its behavior significantly different from that observed by other workers. In effect the shift  $\Delta\lambda$  is proportional to  $T^2$  as found in various microwave studies of films (Ma et al, 1993), and in other ac measurements.

On the other hand our measurements near  $T_c$  differ dramatically from the other work. We have found a mean field like exponent for the temperature dependence of the penetration depth well within the nominal critical region of the phase transition. The microwave measurements of Kamal, *et al.* (1994) have yielded an exponent consistent with the XY model. The mean field result we have obtained is found only if finite-size boundary conditions at the film edge are included in the analysis of the data. If these are omitted, and the film is treated as an infinite plane, then an XY exponent is obtained. Our observation of a mean-field exponent for the penetration depth when the data is analyzed properly can have two interpretations. The first is that the phase transition is

actually mean-field like, despite estimates of the width of the critical region being the order of more than one degree. The evidence from heat capacity studies of XY behavior is actually quite weak (Overend, et al., 1994) considering the number of adjustable parameters going into the analysis. Also the Ginzburg criterion for the critical region is only an approximate condition for the breakdown of mean-field theory. One does not actually know the strength of the inequalities so that the Ginzburg criterion only indicates that mean-field theory has to fail eventually.

The second possibility is far more interesting. Recently a group in Berlin (Kiometzis *et al.*, 1994) predicted that there would be a mean field exponent for the penetration depth even though there were XY-model values for all other thermodynamic exponents including the specific heat exponent. This theory of the phase transition was developed using the tools of gauge field theory. The onset of superconductivity in that language corresponds to spontaneous symmetry breaking via the Anderson-Higgs mechanism. The appearance of a finite penetration depth in this picture corresponds to a nonzero mass associated with the electromagnetic field. This mass then renormalizes away fluctuations associated with the critical behavior of  $\lambda$  to a mean-field critical exponent.

An account of our work has recently been accepted for publication in Europhysics Letters (Lin *et al.*, 1994). A detailed discussion of all of the measurements and techniques associated with the low frequency ac measurements of the impedance of films is contained in the doctoral dissertation of Mr. Z-H. Lin. Various parts of it will be submitted for publication in Physical Review B. The work was presented at the 1995 APS March Meeting.

We have also studied the low frequency (50kHz) conductivity of our films. We have observed an asymmetric peak in its temperature dependence which is similar to those found in the thermal conductivity and microwave surface resistance of single-crystal samples. At present we have no detailed explanation of our observations. They may be due to a competition between the temperature dependence of the inelastic scattering of quasiparticles, which is getting longer as  $T$  is reduced, and the population of quasiparticles, which are freezing out at low temperatures. An account of this work was also presented 1995 APS March Meeting, and is also contained within Dr. Z-H Lin's doctoral dissertation. It is planned to publish the details in Physical Review B.

### 3.4. Properties of Single Crystals of $\text{LuBa}_2\text{Cu}_3\text{O}_{7.8}$ : The Pairing State of High- $T_c$

#### Superconductors

In the course of our early work on magnetic anisotropy and magnetic relaxation in single crystals of high- $T_c$  superconductors we built a modification of the sample holder of a Quantum Design Susceptometer which facilitated the rotation of a sample about an axis perpendicular to the direction of the magnetic field, while at the same time measuring, at the resolution and sensitivity

of the instrument, both the transverse and the longitudinal magnetizations. The ideas for this apparatus have been incorporated in an add-on to the susceptometer which is now offered commercially by Quantum Design. We have used our system over the last two years to study the transverse magnetization (Yip and Sauls, 1992) of the high- $T_c$  superconductor  $\text{LuBa}_2\text{Cu}_3\text{O}_{7.8}$ . The goal of the work was to detect the presence of d-wave pairing which has been inferred from various interpretations of other measurements. In our work the temperature and magnetic field angular dependence of the in-plane transverse magnetization of an untwinned  $\text{LuBa}_2\text{Cu}_3\text{O}_{7.8}$  single crystal has been studied in the Meissner state. The presence of a Fourier component of the signal with angular period  $\pi/2$  would be *prima facie* evidence of d-wave pairing. The observed amplitude and its field-dependence, have been found to be smaller than the theoretical prediction for such pairing. The results are consistent with isotropic pairing, but do not rule out nodeless anisotropic pairing states. This work has been published in Physical Review Letters (Buan et al., 1994), and was reported on briefly at the Magnetism Conference in Minneapolis, at the Aspen Winter Condensed Matter Physics Conference in 1994, at the APS March Meeting in 1994 and at the Grenoble Meeting on superconductivity. It has also been the subject of an invited talk in September 1995 at the Gordon Conference on Superconductivity at Les Diablerets Switzerland. It will be the subject of an invited talk at the 10th Anniversary Workshop on High- $T_c$  Superconductivity to be held in Houston Texas in March 1996.

Recently our attention has been focused on refining the investigations. We have been measuring the magnetization of disk-shaped samples, the use of which eliminates a contribution to the angular dependence of the transverse magnetization with angular period  $\pi$ . This greatly improves the accuracy of the determination of Fourier components with higher angular periods. We have also employed an improved Fourier Transform program which greatly reduces scatter in the analysis. Finally we have been studying the temperature dependence of the angular dependence of the longitudinal magnetization which should yield directly the temperature dependence of the in-plane penetration depth as well as the in-plane penetration depth anisotropy.

As part of our materials characterization effort we have re-commissioned an old  $^3\text{He}$  refrigerator and superconducting magnet system and plan to carry out specific heat measurements in a field which should characterize the magnetic impurity scattering in our crystals as well as provide an independent test of the pairing state.

### 3.5. The Search for High- $T_c$ Superconductivity in the Chevrel Phase Compounds

We proposed to use MBE growth techniques in an effort to enhance by doping with halogen elements the transition temperatures of Chevrel phase compounds to values higher than those reported previously. The proposed doping would change carrier concentrations and thus, in



principle, could move the location of the Fermi level to high peaks in the density of states. If a sufficient increase in the density of states at the Fermi level could be brought about without a change in the crystal structure, then  $T_c$  would be enhanced. The idea of studying doping in the Chevrel phase compounds emerged from the consideration of the implications of the discovery of superconductivity in alkali metal-doped fullerenes, and an attempt to identify potentially similar systems in nature. The Chevrel phase compounds share certain with the fullerenes. These include previous findings of superconductivity, in this case at either low or high transition temperatures, great sensitivity of the transition temperature to doping, the existence of clusters, albeit of molybdenum and sulfur or selenium, rather than carbon, and perhaps a need for a synthesis technique which can produce nonequilibrium stoichiometries, or compositions which would not be formed if conventional bulk fabrication procedures were employed. The concept that doping Chevrel phase compounds could be a means of elevating their transition temperatures is made plausible if one notes the remarkable change in the transition temperature of  $\text{Mo}_6\text{S}_8$ , from 1.7 K to 14 K when two S atoms are replaced by I to yield  $\text{Mo}_6\text{S}_6\text{I}_2$  (Chevrel and Sergent, 1982). A similar result was obtained with Se compounds. The specific approach of enhancing superconductivity in the Chevrel phase compounds by doping, although arrived at by the investigator in the context of emulating the mechanism for superconductivity in the fullerenes, was actually considered in a discussion between A. H. Freeman, B. T. Matthias, and P. W. Anderson, following a talk by Freeman, at a meeting on ternary superconductors more than a decade ago. The idea was never pursued, certainly not within the context of thin film synthesis.

We reconfigured our older MBE machine to carry out the growth of halogen-doped Chevrel phase compounds. This involved replacing the bell jar, and reworking the electron guns and internal fixturing to permit *in situ* RHEED studies. After several trials with the sulfur compound, we switched to using selenium, which is less volatile and easier to prepare. Thin films of Mo-Se and Mo-Se-I were deposited onto single-crystal  $\text{Al}_2\text{O}_3$  substrates. The films obtained were characterized by X-ray diffraction, atomic absorption spectroscopy, and magnetic measurements. Phases of Mo and  $\text{MoSe}_2$  were identified in the resultant films. Reproducible fabrication of  $\text{Mo}_6\text{Se}_8$  and  $\text{Mo}_6\text{Se}_6\text{I}_2$  was not successful, most likely because of the high volatility of the selenium and iodine at the high substrate temperatures needed to carry out the required reactions. It was not possible to increase the fluxes of these elements enough to overcome this difficulty. Films deposited at substrate temperatures of  $700^\circ\text{C}$  revealed traces of the  $\text{Mo}_6\text{Se}_8$  phase, but magnetic measurements did not show diamagnetic response at low temperatures in these films. Adding iodine to the films during deposition did not change the composition and phase distribution of the films. After a total of sixty two runs in an attempt to achieve the goals of this project, we suspended the activity to devote our resources to other directions of research. Further progress might be possible with substantially increased substrate temperatures, and techniques for ionizing

the sulfur and iodine fluxes to enhance their reactivity. This would require substantial additional investment which would have diverted resources from more successful parts of the program.

### 3.6 Colossal Magnetoresistance in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and Cuprate/manganite Heterostructures

Giant magnetoresistance (GMR) has been a very active area of research for the last few years and has been observed in a variety of metallic systems, mainly the metallic multilayers. The decrease in the resistance has been attributed to spin-dependent interface scattering between the ferromagnetic and non-magnetic regions. Perovskite-like orthomanganite oxides such as the  $\text{La}_{1-x}\text{M}_x\text{MnO}_3$  compounds, where  $\text{M}=\text{Ba}$ ,  $\text{Sr}$ ,  $\text{Ca}$ , and  $\text{Pb}$  have an intrinsic spin structure similar to that of the metallic multilayers which exhibit GMR. The spins are aligned ferromagnetically in the Mn-O layers and antiferromagnetically between the layers. This suggests the possibility of observing the magnetoresistive effect for these materials. Films of La-Ca-Mn-O, La-Sr-Mn-O and La-Ba-Mn-O have been grown by sputtering (Chura, *et al.*, 1993) and laser ablation (Jin *et al.*, 1994 and von Helmolt *et al.*, 1993). Initial efforts yielded magnetoresistance values of about 50% for as-deposited films at temperatures between 200 K and 300 K depending on the process conditions. Recently, a thousand-fold decrease in resistance was obtained in an epitaxially grown film of La-Ca-Mn-O which was post annealed to obtain the highest magnetoresistance value (Jin *et al.*, 1994). However, the origin of this "colossal magnetoresistance" (CMR) is not presently understood as it seems to be extremely dependent on the processing conditions.

We have grown epitaxial thin films of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3\pm d}$  ( $x=0.33$ ,  $0.4$  and  $0.5$ ) on  $\text{SrTiO}_3$  (100) substrates using ozone assisted (MBE, a method which has been used successfully for the growth of high quality superconducting oxide thin films. The substrate temperature was around  $680^\circ\text{C}$  and the ozone partial pressure was maintained at approximately  $1 \times 10^{-5}$  Torr. We employed a sequential deposition technique, namely, block-by-block deposition (BBD) for the growth of these films. BBD has been shown to be an effective technique for reducing the number of defects such as the undesired, second-phase precipitates for the growth of complex, multicomponent films where a multitude of phases can form (Locquet *et al.* 1994 and Locquet and Machler, 1994). The growth was dynamically monitored using *in-situ* RHEED.

The chemical composition of the films were analyzed by inductively-coupled plasma mass spectroscopy and Rutherford backscattering analysis which were found to be consistent. *In-situ* RHEED and high resolution x-ray diffraction (Philips MRD) analyses showed that the films grew epitaxially on  $\text{SrTiO}_3$  with a cube-on-cube arrangement. The lattice constants were between  $3.84 - 3.88 \text{ \AA}$  depending on the doping  $x$ . No secondary phases were observed by structural analyses.

The electrical and magnetic properties of the films were measured using a SQUID susceptometer (Quantum Design) which is equipped with a superconducting magnet with the maximum capable field of 5.5 T. A specially designed probe was used for electrical measurements

in the magnetometer. The electrical measurements were made using a conventional four-point technique.

Figure 6 shows the magnetic and the resistive transitions in nominally zero magnetic field ( $\approx 2$  G) of a 150 unit cell thick ( $\approx 580$  Å)  $\text{La}_{0.52}\text{Ca}_{0.47}\text{MnO}_{3\pm d}$  film. The resistance increases as the temperature decreases (semiconductor-like behavior) and reaches a maximum at 248 K and then decreases to a value about two orders of magnitude lower than the peak resistance (metallic behavior). The magnetization increases sharply around 248 K, which is also the resistive peak temperature, suggesting that the film undergoes a ferromagnetic transition.

The peak in the magnetoresistance, however, seems to correspond to the peak in the  $dR/dT$ , the differential resistance at zero applied magnetic field. This suggests that the resistance peak may be due to spin-disorder scattering. Figure 7 shows a plot of the differential resistance at zero field and the magnetoresistance (MR) for an applied field of 300 G. MR is defined as  $\frac{1-R(H=300)}{R(0)}$ , where  $R(H)$  is the resistance at a magnetic field of 300 G and  $R(0)$  is the resistance at zero field. It can be seen from the figure that the MR peak occurs at  $T \approx 230$  K.

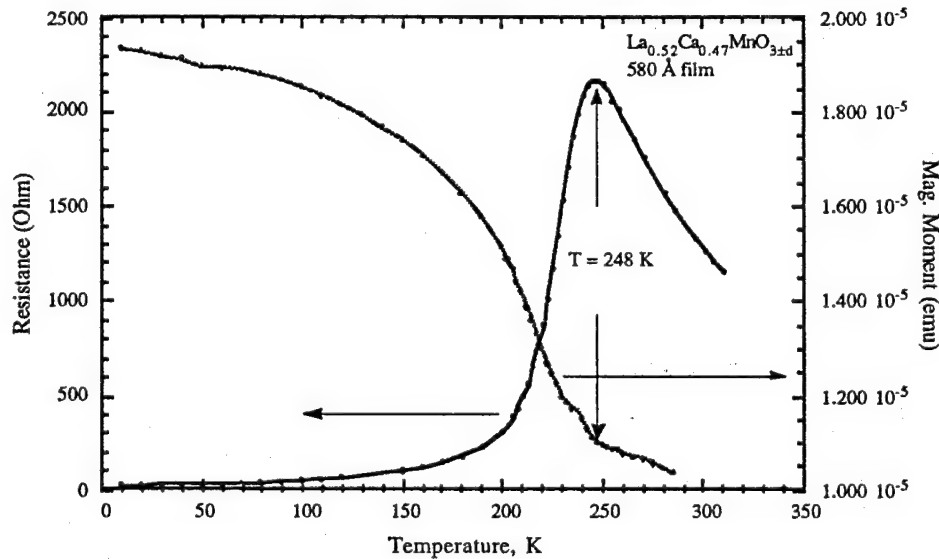


Fig. 6. Plot of the resistive and magnetic transition in nominally zero magnetic field.

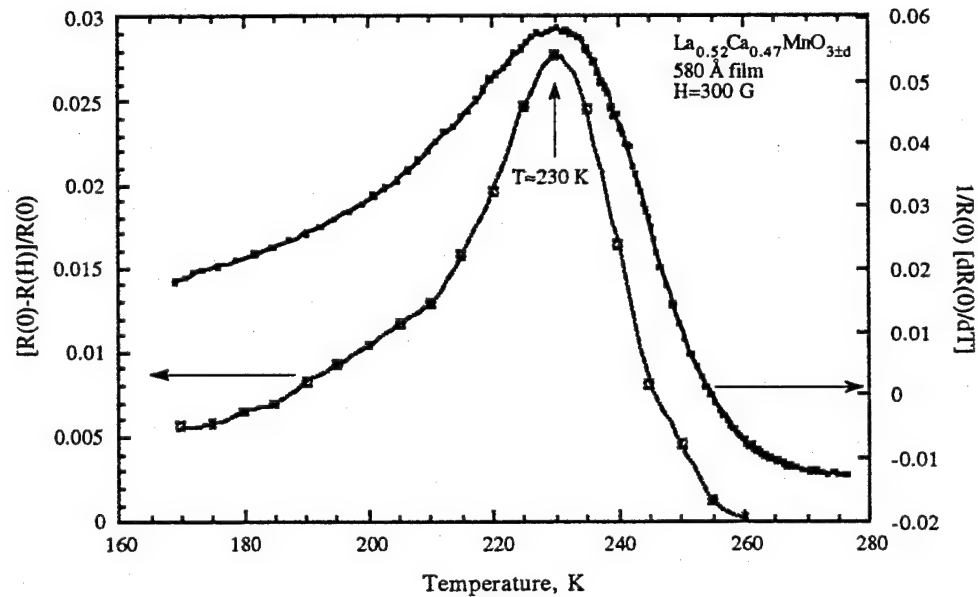


Fig. 7. Comparison of the temperature dependence of the differential resistance and the magnetoresistance.

The variation of normalized resistance  $\frac{R(0)}{R(H)}$  with applied magnetic field is shown in Fig. 8 for the same film at a temperature,  $T=230$  K, corresponding to the maximum magnetoresistance. The resistance appears not to saturate with increasing field up to a field of 5.5 T. The resistance decreases with magnetic field as a power law with an exponent of -0.67 in the region between 1 T and 5.5 T. If we estimate the magnetoresistance normalized to the high field value, i.e.,  $\frac{R(0)-R(5.5T)}{R(5.5T)}$ , then we obtain the magnetoresistance to be  $\approx 400\%$ . This value is higher than any published in the literature for an as-deposited film (Jin *et al.*, 1994 and von Helmolt, *et al.* 1993). It is worthwhile to note that the highest values of MR were obtained only after post-deposition annealing treatments.

The temperature dependence of the magnetization was studied for different applied fields in order to obtain a better understanding of the magnetic transition. Figure 9 shows the magnetization data for an applied field of 50 G. The zero field-cooled and field-cooled curves are different below the temperature,  $T=215$  K. Studies are in progress to understand the origin of the irreversible behavior in these films.

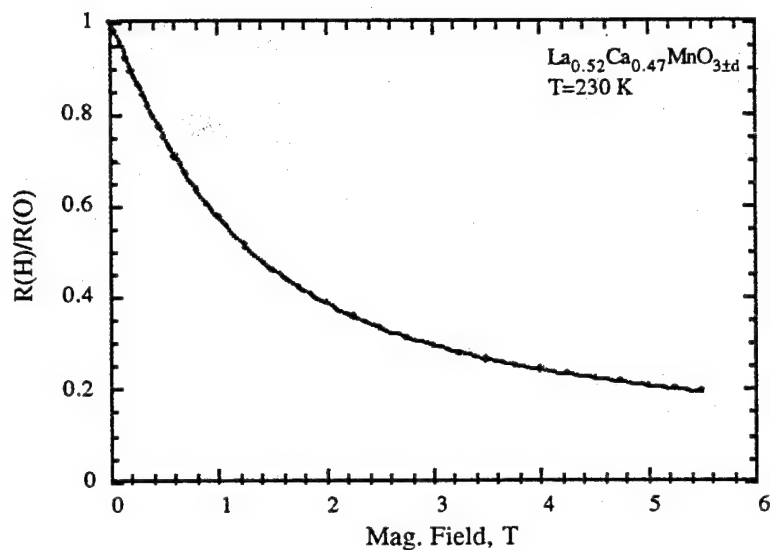


Fig. 8. Variation of the normalized resistance with applied magnetic field at 230K.

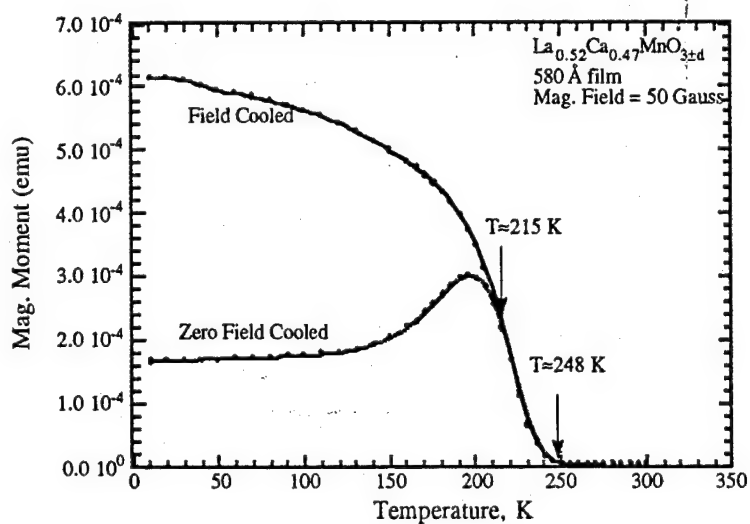


Fig. 9. Zero-field-cooled and field-cooled magnetization curves in a field of 50G.

We view this research as an example of what one can do with the BBD technique which is extremely versatile and applicable to a wide range of technically and scientifically interesting oxide

materials. We should note that we have also prepared  $\text{Dy}_{1-x}\text{Ca}_x\text{MnO}_3$  which turns out to be an insulator which is lattice-matched to the 123 compounds. This material could serve as a barrier in a tunneling junction or as a general purpose insulator in a process technology involving the 123 compounds.

Our most recent results have involved the successful growth of the compound  $\text{La}_{1/2}\text{Sr}_{1/2}\text{MnO}_3$  by the BBD method, and the production of heterostructures of  $\text{La}_{1/2}\text{Sr}_{1/2}\text{MnO}_3$  combined with  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ , in which both the onset of ferromagnetism and the onset of superconductivity have been observed. Given the remarkable smoothness of perovskite manganite films, as shown in Fig. 10, this result should facilitate research on the injection of spin-polarized carriers into high- $T_c$  superconductors which has been proposed for the next grant.

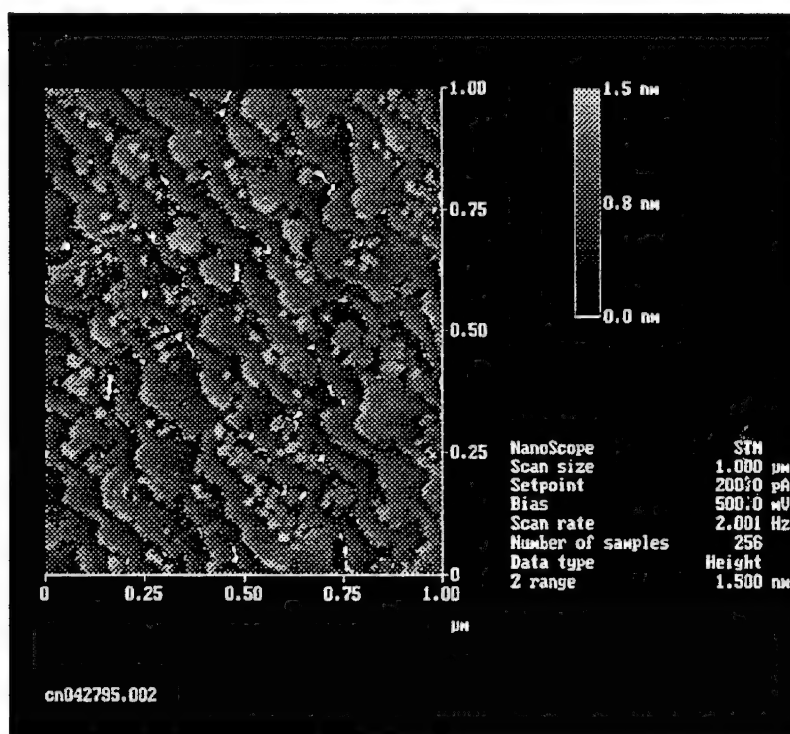


Fig. 10. STM scan of  $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$  area of a Perovskite Manganite film showing  $1000\text{ \AA}$  wide terraces which are many microns in length.

Work on perovskite manganites has been the subject of two manuscripts, one already published in Applied Physics Letters, and a second, recently submitted. work on the cuprate/manganite heterostructures will be reported at the 1996 APS March Meeting in St. Louis.

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## 5.0. Personnel

V. S. Achutharaman <sup>a</sup>	Research Assistant and then Research Associate in Chemical Engineering and Materials Science
Anon Bhattacharya	Research Assistant in Physics
Allen M. Goldman	Professor of Physics
Daniel Grupp	Research Associate in Physics
Phillip Krause	Department of Education Fellow, Research Associate in Physics (AASERT)
Zhong-Heng Lin <sup>b</sup>	Research Assistant in Physics and Department of Education Fellow
Edmund Nowak <sup>c</sup>	Research Assistant in Physics
Catherine Nordman <sup>d</sup>	Research Assistant in Electrical Engineering
Adele Ruosi <sup>e</sup>	Italian Government Fellow (University of Naples)
Gabriel Spalding <sup>f</sup>	Research Associate in Physics
Vladislav Vas'ko	Research Assistant in Physics

<sup>a</sup> Present address: Materials Science Corporation, Sunnyvale, CA

<sup>b</sup> Present address: Connor Peripherals, Milpitas, CA

<sup>c</sup> Present address: James Franck Institute, University of Chicago

<sup>d</sup> Present address: MITI Corp., Minneapolis, MN

<sup>e</sup> Present address: Department of Physics, University of Naples

<sup>f</sup> Present address: Department of Physics, Haverford College

## 6.0. Collaborators

Robert Shelton	Professor of Physics, University of California-Davis
Chen-Cher Huang	Professor of Physics, University of Minnesota
Oriol T. Valls	Professor of Physics, University of Minnesota
Benjamin Bayman	Professor of Physics, University of Minnesota
John S. Buan	Research Assistant in Physics
Branko Stojkovic	Research Assistant in Physics
S. Sridhar	Professor of Physics, Northeastern University
N. Israeloff	Assistant Professor of Physics, Northeastern University
T. Jacobs	Graduate Student, University of Karlsruhe

## 7.0 Doctoral Dissertations

"Growth and Structure of High Temperature Superconducting Thin Films," V. S. Achutharaman, December 1993 (Materials Science)

"Studies of the High- $T_c$  Superconductor  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  Using Low Temperature Scanning Tunneling Microscopy," Jin-Xiang Liu, September 1993 (Physics)

"Voltage Noise As a Probe of Vortex Kinetics in High Temperature Superconductors," Edmund Richard Nowak, February 1994 (Physics)

"Superconducting and Magnetic Device Development Using Oxide Materials," Catherine Nordman, July 1995. (Physics)

"Temperature Dependence of the Electromagnetic Penetration Depth of High Temperature Superconductors," Zhong-Heng Lin, July 1995. (Electrical Engineering)